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Automatic Control of a Closed Conduit Cutback Irrigation System

Richard E. Kraft

ESTIMATION OF PLANT S AND ZN CONCENTRATION BY SOIL TEST CORRELATION

BY

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ESTIMATION OF PLANT S AND ZN CONCENTRATION

BY SOIL TEST CORRELATION

This thesis is approved as a creditable and independent investigation by a candidate for the degree, Master of Science, and is acceptable as meeting the thesis requirements for this degree. Acceptance of this thesis does not imply that the conclusions reached by the candidate are necessarily the conclusions of the major department.

Thesis Adviser Date

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INTRODUCTION

Sulfur and Zn are two elements essential for plant growth. Deficiencies of these two plant nutrients occur commonly in many areas of the world.

Zinc deficiency symptoms were noted in corn in South Dakota during the late nineteen fifties (19). In the summer of 1970, S deficiency symptoms appeared in corn (Zea mays L.) grown on sandy soils in Marshall County, South Dakota (60).

Zinc deficiencies of corn occur more often when corn is grown on soils that are characterized by one or more of the following properties: sandy texture, low organic matter, severe past erosion, leveled for irrigation, high lime level, or high P level.

Sulfur deficiencies are more prominent in corn and legumes. Sulfur deficiencies are commonly associated with the following soil properties: low organic matter, sandy texture, or acid soil reaction.

One of the problems related to knowing which soils need S and Zn fertilizer applications for agricultural crops is the establishment of soil tests which predict the S and Zn supplying status of the soil. A soil test for a particular nutrient can be calibrated by correlation of soil tests with plant nutrient concentration, plant nutrient uptake, dry matter yield, or grain yield.

A preliminary study conducted by Ward, Pfeifer, and Carson (60) revealed that there was a need for a S extracting procedure. More work was needed to find a test giving values more closely correlated with plant S concentration under South Dakota conditions.

South Dakota State University presently uses a 0.1N HCl extraction procedure for soil Zn determinations. Since several new methods for soil Zn determinations have been developed recently, an evaluation of these new procedures under South Dakota conditions was considered necessary.

The main objective of this study was to establish Zn and S soil tests that predict the Zn and S supplying status of South Dakota soils. The Zn and S supplying abilities were determined by measuring corn yield responses to an application of Zn or S and by measuring the nutrient concentration levels in the corn plants at two stages of growth.

Another objective was to determine yield response of corn from the addition of Zn and S on soils in the Brown and Marshall County area of South Dakota.

LITERATURE REVIEW

Sulfur and Zn levels in soils are influenced by many factors. These factors must be considered when attempting to establish soil tests that will best reflect the soils ability to supply S and Zn to plants. Some factors affecting S and Zn availability and some methods of determining S and Zn availability will be discussed in the following review.

SULFUR

Factors Influencing S Availability

Organic Matter and C:N:S Ratio

Starkey (51) postulated that over half of the S in the surface layer of most soils occurs in the organic fraction. Donald and Williams (21) suggested that the close relationship between total S and total N was due to most of the soil S being in the organic form.

Walker and Adams (58) found a C:S ratio of 120:1.3 in samples of grassland soils taken to a depth of 53 cm. The N:S ratio was 10:1.3 and was remarkably constant which suggests that most of the S was in the organic form. Later work by Williams, Williams, and Scott (66) showed similar C:S and N:S ratios. They observed that both C and N were highly correlated with S in the soil and that the calcareous soils had lower C:N ratios than noncalcareous soils.

Harward, Chao, and Fang (28) worked with alfalfa (Medicago sativa L.) in a greenhouse experiment and discovered that there was a close

relationship between the percent S and percent N content of the alfalfa plants. Pumphrey and Moore (44) expanded this and revealed that no significant yield increases were obtained from S fertilization where non-fertilized alfalfa forage had a N:S ratio smaller than 11:1. They stated that the N:S ratio of the forage predicted the need for S fertilization 96 percent of the time. Barrow (3) found that the amount of S mineralized depended on S content and C:S ratio of decomposing organic materials. He discovered that C:S ratios of 200:1 and 420:1 were minimum and maximum ratios at which no mineralization of S occurred.

Depth in Profile

Jordan and Bardsley (34) found the distribution of extractable S in the soil to increase with increasing depth. Surface horizons were found to contain 3 ppm or less extractable S and the zone of S accumulation varied from 15 to 76 cm below the surface.

Kamprath, Nelson, and Fitts (35) observed S deficiency symptoms in tobacco (Nicotiana tobaccum L.) and cotton (Gossypium hirsutum L.) early in the growing season. Later in the season the symptoms disappeared in tobacco but not entirely in cotton. They proposed that tobacco was able to utilize adsorbed SO_4-S at greater depths since it has deeper rooting characteristics than cotton. According to a study conducted by Sanford and Lancaster (46), SO_4-S in the subsoil tended to exceed that in the corresponding surface soil. Williams and Steinbergs (64) found that most surface soils had a low capacity for SO_4-S adsorption. However, many acid subsoils adsorbed SO_4-S very strongly.

pH and Other Plant Nutrients

In 1963 Chao, Harward, and Fang (15) conducted an experiment on the effects of cations on SO_4-S adsorption. They found that the influence of different cations on SO_4-S adsorption was associated with two factors, the nature of the cation and the pH of the soil solution. However, pH appeared to be the dominating factor influencing SO_4-S adsorption. Work carried out in Australia with acid and calcareous soils (64) indicated that SO_4-S adsorption was negligible above pH 6.5.

Chao (14) found that all anions with the exception of $C_2H_3O_2^{-1}$, AsO_3^{-3}, BO_3^{-3}, Cl^{-1}, NO_3^{-1} and SiO_4^{-4}, depressed So_4-S adsorption, It was determined that PO_4^{-2}, MoO_4^{-2}, and F^{-1} were the most effective anions for decreasing SO_4-S adsorption. Hydroxide and HCO_3^{-1} anions decreased SO_4-S adsorption but this effect was attributed to a change in soil pH. Anionic factors affecting SO_4-S adsorption were; competition for anion exchange site, ability of anions to form chelate complexes with Fe and Al, and precipitation reactions.

Several studies have been carried out concerning the effect of S on Mn in the soil. Tisdale and Bertramson (54) suggested that application of S may be used to correct a lime induced Mn deficiency in soybeans (Glycine max L.). Work by Garey and Barber (26) revealed that added elemental S created three reactions in the soil; an oxidation-reduction reaction, an increase in SO_4^{-2} concentration, and a decrease in pH. Sulfur oxidation appeared to give yields and Mn contents above that which could be attributed to a decrease in pH. Hoeft and Sorenson (30)

worked with three Nebraska soil types and observed that added S increased Mn concentration of corn plants in only one of the three soils. They proposed that the other two soils had a greater buffering capacity, therefore Mn availability did not increase because soil pH did not decrease.

Soil Texture

Sulfur deficiencies are found more often on sandy textured soils than on finer textured soils (25). A study conducted by Bardsley and Lancaster (2) with several Mississippi surface soils of different textures revealed that organic S and reduced inorganic S (reserve S) plus SO_4-S were progressively more as percent sand decreased and percent clay increased. Neller (42) found that the amounts of SO_4-S increased with increased clay concentration of soil in a highly significant manner. The correlation coefficient (r value) for percent clay x ppm SO_4-S was 0.82.

Determination of S Availability

Soil Tests

As early as 1928, it was discovered that only a small fraction of the total soil S occurred in the SO_4-S form (45). Bentley, Hoff, and Scott (7) reported that total S content of soil was not a suitable means of predicting responsiveness of plants to S fertilization.

Williams and Steinbergs (65) confirmed that adsorbed SO_4-S was readily available to plants due to a measured decrease in adsorbed soil

SO_4-S following the growth of oats (Avena sativa L.). In a similar study Barrow (4) found that the decrease in extractable soil S was precisely related to the measured uptake of S by soft brome (Bromus mollis L.) in the greenhouse for 183 days. The close relationship between the amount of S extracted with a 0.1M $CaH_4(PO_4)_2 \cdot H_2O$ extractant and the amount of S taken up by the plant could be explained by the observation that mineralization of S appeared to be lower when plants were growing in the soil.

Katta and Lynd (36) in a laboratory study observed that growth response of Aspergillus niger was closely correlated to soil SO_4-S levels. However, Cooper (18) found that water-soluble SO_4-S, total S, and organic S did not correlate well with field trials and that bio-assays using Aspergillus niger and Chorella sp as indicator organisms gave variable results even under standardized conditions.

Spencer and Freney (50) compared the following soil S extraction procedures with one another: cold-water-extractable, phosphate-extractable, acetate-extractable, hot-water-extractable, and heat-soluble (evaporated to dryness and heated for one hour at 102 C and then extracted with NaCl). They found that the phosphate-extractable SO_4-S procedure (KH_2PO_4 containing 500 ppm P) was superior to the other extractants tested on the basis of its ability to displace adsorbed SO_4-S. However, in two soils from low rainfall areas containing free gypsum, less SO_4-S was extracted by this extractant than by water due to the solubility of gypsum being suppressed by phosphate ions.

Williams and Steinbergs (63) studied several soil S fractions including total S, water-soluble SO_4-S, and heat-soluble S. They found the best correlation of S uptake by oats grown in pot cultures with heat-soluble S, and the poorest correlation of S uptake with water-soluble SO_4-S. Spencer and Freney (50) revealed that correlations between heat-soluble S, cold-water-extractable SO_4-S, or hot-water-extractable SO_4-S and plant growth response to applied S were weak. Plant growth responses were strongly correlated with Aspergillus niger-extractable S and phosphate-extractable SO_4-S.

Ensminger and Freney (23) reviewed S extraction procedures prior to 1966. Solutions containing phosphate ions appeared to be the best extractants for determining available S. Research by Fox, Olson, and Rhoades (25) in Nebraska suggested that extractants containing phosphate ions appeared to apply very well over a wide range of soil types. They found that $Ca(H_2PO_4)_2$ was more convenient than KH_2PO_4 since filtration was more rapid and turbid extracts less frequent.

Cooper (18) compared several S extraction procedures and found that a sodium phosphate-acetic acid extractant was the most effective in differentiating between responsive or non-responsive soils.

Recent work in Wisconsin (31) indicated that $Ca(H_2PO_4)_2 \cdot H_2O$-HOAc gave the most reliable estimate of S availability. Calibration of this test was as follows: less than 6.1 ppm S, response expected; 6.1-9.0 ppm S, response possible; and greater than 9.0 ppm S, response not expected.

Plant Tests

Walker and Bentley (59) analyzed several legumes for three S fractions in order to determine the usefulness of these fractions for indicating the need of S fertilizer. They concluded that the S needs of plants were indicated more by extractable S or extractable SO_4-S in plants than by total S or by N-S ratios in plants.

There is some controversy concerning the best time to sample plants as well as which plant parts to sample. Fox, et al. (24) stated that leaves sampled at an early stage of growth were superior to those sampled late for evaluating S status of corn. However, other workers (33, 17) have proposed that corn leaf samples taken at silking are better indicators of nutrient status of corn than leaf samples taken at earlier growth stages. Eaton (22) found that SO_4-S generally appears to increase with leaf age while organic S tends to decrease.

ZINC

Factors Influencing Zn Availability

Soil pH

Wear (61) conducted a study on the effect of pH and Ca on Zn uptake by plants. He found that additions of $CaCO_3$ and $NaCO_3$ to soils reduced Zn uptake while added $CaSO_4$ increased Zn uptake. Since $CaCO_3$ and $NaCO_3$ increased soil pH while $CaSO_4$ decreased soil pH, he

concluded that reduced Zn uptake by plants was a pH effect not a Ca effect.

Boawn, et al. (9) studied the effects of three N carriers; $(NH_4)_2SO_4$, NH_4NO_3, and $Ca(NO_3)_2$ on Zn uptake by potatoes (Solanum tuberosum L.), sorghum (Sorghum bicolor L. Moench), and sugar beets (Beta vulgaris L.). When a N carrier changed Zn uptake it was found to be related to whether the carrier increased or decreased soil pH. Zinc uptake increased as soils became more acid and decreased as soils became more alkaline.

Terman, Allen, and Bradford (53) studied Zn responses on Hartsells fine sandy loam. They discovered a high correlation ($r = 0.97$) between corn forage yields on soils without applied Zn and depression of soil pH by applied fertilizers. In a later study, Shukla and Morris (49) found that liming two Georgia soils resulted in decreased corn growth, plant Zn concentration, and Zn uptake.

Sharpless, Wallihan, and Peterson (48) studied Zn retention in arid soils. They concluded that more Zn was usually retained when CEC and pH were increased.

Soil Organic Matter and Zn in the Soil Profile

Dolar and Keeney (20) found an increase in uptake of Zn, Mn, and Cu by oats with an increase in native soil organic matter. A multiple regression analysis carried out by Udo, Bohn, and Tucker (56) on 10 calcareous Arizona soil samples showed that organic matter

was highly associated (R = 0.87) with the total soil Zn concentration. In the same study clay concentration was also shown to be related to total Zn (r = 0.71).

Himes and Barber (29) discovered that organic matter reacted with divalent metal ions in a manner similar to chelation reactions. They found that removal of organic matter by oxidation with H_2O_2 destroyed the ability of the soil to chelate Zn. Another study (41) revealed that water extracts of three types of organic matter contained complexing agents capable of removing Zn from soils. These compounds complexed Zn that could not be removed by either water or 2.0N KCl.

Zinc deficiencies have been associated with severly eroded soils or soils leveled for irrigation (27). This was attributed to removal of topsoil high in organic matter and exposure of subsoil having a higher pH and lower organic matter.

Phosphorus and Other Plant Nutrient Effects

Boawn and Brown (8) used four P concentrations in solution; 0, 2.2, 4.4, and 8.8 ppm. Through trial and error enough Zn as $ZnSO_4 \cdot 2H_2O$ was added to the soil medium until only those plants receiving the 8.8 ppm P solution showed a Zn deficiency. In both the beans (*Phaseolus vulgaris* L.) and potatoes P induced a Zn deficiency without causing a decrease in the Zn concentration of the plants. Normal plant

growth was increased at any given P level. The results of their experiment tended to support the view that the P-Zn interaction is physiological in nature.

Deibert (19) conducted a greenhouse experiment on several South Dakota soils. His results indicated that high rates of applied P fertilizer reduced Zn concentration and yield of corn plant tops on a soil high in extractable P and low in extractable Zn.

Martin, McLean, and Quick (40) found that soil temperatures were important in determining if large applications of P induced Zn deficiencies. Applied P induced more Zn deficiencies at lower soil temperatures. Their results revealed that as soil temperatures were progressively increased from 10 to 27 C there was less benefit from added Zn associated with high P treatments. However, on soils severely deficient in Zn, P induced Zn deficiency symptoms were evident at all temperatures.

Dolar and Keeney (20) observed that uptake of Zn, Mn, and Cu tended to decrease in soils having high native P and an adequate supply of N and K.

Soil Texture

Bauer (6) observed that Zn deficiency symptoms of corn in southeastern North Dakota were usually found on coarse to moderately-coarse textured soils.

Wear and Evans (62) studied the relationship of Zn uptake in corn and sorghum to three soil Zn extracts. They found that extractable Zn tended to increase as soil texture became finer.

Determination of Zn Availability

Soil Tests

Martens, Chester, and Peterson (39) worked with several Zn extractants. Relative amounts of Zn extracted by Zn tests were found to be in the order, *Aspergillus niger* > 0.1N HCl > dithizone > 0.2M $MgSO_4$. *Aspergillus niger* was equated with total Zn in predicting Zn uptake by plants since they extracted a fixed fraction of total Zn. Martens, Chester, and Peterson (39) concluded that the extra Zn extracted by 0.1N HCl over dithizone extracted Zn was not available to plants. Clay and organic C were more related to 0.1N HCl-extractable Zn than to 0.2M $MgSO_4$-extractable Zn which suggests that 0.2M $MgSO_4$ measures solution and readily exchangeable Zn.

Nelson, Boawn, and Viets (43) used a lime determination in conjunction with acid extraction of soil Zn by 0.1N HCl. They found little or no Zn extraction by 0.1N HCl in calcareous soils until all lime was reacted with HCl and soil pH was reduced to 5.0 or lower. They concluded that lime determinations were just as effective as a titration curve for obtaining titratable alkalinity. They obtained a good separation of Zn deficient vs. non-deficient soils from seven western states.

. Wear and Evans (62) conducted a growth chamber experiment with 12 medium- to coarse-textured soils. Three soil Zn extractants; 0.05N HCl + 0.025N H_2SO_4, 0.1N HCl, and 0.05M EDTA (ethylenediaminetetraacetic acid) at pH 7.0, were correlated with plant uptake of Zn in corn and sorghum. Correlation coefficients of Zn tests with plant Zn uptake were as follows: 0.89, 0.82, and 0.62 for corn and 0.70, 0.63, and 0.44 for sorghum respectively. Brown, Krantz, and Martin (11) worked with 53 California soils and found the critical level of dithizone-extractable Zn to be 0.55 ppm. Eighty-four percent of the soils containing amounts less than this level responded to Zn application and 76 percent of the soils containing greater than this amount did not respond. However, in a later study conducted by Trierweiler and Lindsay (55) on 42 Colorado soils, the critical level for distinguishing responsive from non-responsive soils with dithizone was 0.95 ppm. In this same study Trierweiler and Lindsay found the critical level for the EDTA-$(NH_4)_2CO_3$ extractant to be 1.4 ppm Zn. They were not successful in determining a critical level for 0.1N HCl. From their results they concluded that the EDTA-$(NH_4)_2CO_3$ extractant was superior to 0.1N HCl and dithizone on the basis of correlation with plant Zn uptake. It was also found to be well adapted to neutral and high lime soils.

Lindsay and Norvell (38) developed a new chelating method for extracting soil Zn. The extract consists of DTPA(diethylenetriaminepentaacetic acid)-TEA(triethanolamine), and $CaCl_2$ adjusted to pH 7.3.

The following calibration levels were established: 0-0.50 ppm, low; 0.51-1.00 ppm, marginal; and 1.01 + ppm, adequate.

Brown, Quick, and Eddings (12) compared DTPA-extractable Zn with 0.1N HCl, Na_2 EDTA, and dithizone-extractable Zn. The chance of predicting corn plant response in a greenhouse experiment was 83 percent for DTPA, 79 percent for dithizone, 73 percent for 0.1N HCl, and 72 percent for Na_2 EDTA. They also found that in 80 percent of soils containing 0.50 ppm or less DTPA-extractable Zn, there was an increase in plant growth due to applied Zn. Above 0.50 ppm Zn only 15 percent of the soils responded to additional Zn and above 1.35 ppm Zn no response was obtained. It was concluded that DTPA was the best extractant of available Zn on the basis of a better prediction for separating responsive from non-responsive soils.

Plant Tests

Chapman (16) stated that the great spread in Zn concentration of leaves, where deficiency is characterized by low values and excess by high values, is a sound basis for using plant analysis for assessing the Zn status of plants. He listed the levels where corn began to show deficiency symptoms as 9.0-9.3 ppm on the lower leaves at tasseling time and 14.6-15.1 ppm on leaves at the sixth node from the base at silking. Jones (33) categorized the Zn status of the corn ear leaf at silking as follows: $\leq$ 10 ppm deficient, 11-20 ppm low, 21-70 ppm sufficient, 70-100 ppm high, and $>$ 100 ppm excess. Chapman (17) in

another study reported the following values for the corn leaf just opposite and below the ear at full tassel: low, < 20 ppm; intermediate, 25-100 ppm; high, > 200 ppm.

METHODS AND MATERIALS

Field experiments were established at eight locations in northeastern South Dakota to obtain correlation data for Zn and S soil tests. Another objective was to determine the yield response of corn to the addition of Zn and S fertilizer.

Field Procedure

The experiments were conducted with corn at five locations in Marshall County and three locations in Brown County.

Since the sites were established on privately owned land, an effort was made to select farmers that had demonstrated better than average management ability. The plots were designed so the farmer could manage them in the exact manner as the remainder of his field. Table 1 lists various management practices carried out at each site.

The treatment areas were 6.1 meters wide and 18.3 meters long. The treatments were as follows:

1. 22.4 kg of S/ha, no Zn.
2. 22.4 kg of S/ha, 16.8 kg of Zn/ha.
3. no S, 16.8 kg of Zn/ha.
4. no Zn, no S.

All plot areas received 16.8 kg of N/ha, 22.4 kg of P/ha, and 44.8 kg of K/ha in addition to the fertilizer applied by the cooperators.

The treatments were replicated four times at each location. The replicates were arranged in non-adjacent fashion near a field boundary.

Table 1. Cooperator management practices at seven field locations.

Cooperator	Planting Date	Planting Rate Seeds/ha	Corn Variety	Row Spacing cm	Planting Method	Herbicide kg/ha	Insecti-cide	Fertilizer N+P+K, kg/ha	Application method
Symmens	May 13	44,000	Sokota TS 49	96	List	Ramrod 5.6	Aldrin 5.6 kg/ha	17+18+12 112+0+0	Starter broadcast
Zuehlke	May 6	42,000	Pioneer 3956	96	Top plant	Ramrod 9.0	Heptachlor with seed 322 g/hl	78+13+16	Starter
Jarret	May 19	49,000	Trojan TXS 93	76	List	Ramrod 11.2	None	13+20+0 94+0+0	Starter broadcast
Moeckley	May 4	57,000	Trojan TX 90	96	Shallow List	Atrazine and oil 1.1	Aldrin 5.6 kg/ha	8+9+0 74+0+0 18+20+0	Starter broadcast
Finley	May 14	54,000	Acco U 323	96	Top plant	None	Ortho Isotox with seed 322 g/hl	25+11+7	Starter
Dinger	May 19	54,000	Pioneer 3862	76	Top plant	Atrazine 1.1	Aldrin 5.6 kg/ha	17+26+0 101+0+0	Starter broadcast
Spurr	May 9	44,000	Pioneer 3956 A	76	List	Ramrod 5.9	Aldrin 7.3 kg/ha	9+12+13 104+0+0	Starter broadcast
Fisher	Data not taken - plot abandoned								

The non-adjacent placement of replicates within locations was done to obtain as much variation as possible in soil test values for Zn and S.

Prior to the application of the treatments, soil samples were taken within each replicate to a depth of 122 cm. Composite subsamples from three soil cores were taken for the following depths: 0-15, 15-30, 30-61, 61-91, and 91-122 cm.

Plant samples were taken twice during the growing season from each treatment within each replicate. The first samples were taken when the corn plants were at the 5-6 leaf stage of development. The most fully matured leaf of 10 corn plants was sampled. The second sampling was done at tasseling stage. The leaf opposite and below the ear of 10 corn plants was sampled.

The Finley location was excessively weedy and lacking in N so at the time of the second leaf sampling this plot was weeded by hand and N was added at a rate of 112 kg of N/ha.

Yield samples were taken the last week in September. Yields were determined by harvesting two rows 12.2 meters in length down the center of the treatment area. Corn was weighed in the field and subsamples were taken back to the laboratory for moisture determination.

At the Fisher location two different corn hybrids were planted in the plot areas. Also, the fertilizer applicator on the corn planter was not working properly so that some areas within the plots received little or no additional N and P. Based on these problems, this location had to be sacrificed since there was no way to accurately measure the influence of these uncontrolled variables.

Laboratory Procedure

The soil samples were air-dried, ground, and sieved through a 2-mm mesh sieve.

Organic matter was determined using Graham's modification of the Walkley and Black procedure as outlined by Jackson (32).

Water soluble NO_3-N was extracted with a soil to water ratio of 1:3. The samples were shaken for five minutes on a rotational shaker. A small amount of CaO was added to obtain a clear filtrate. Nitrate-N was determined by the phenoldisulfonic acid-colorimetric method of Bremner (10).

Soil P was extracted with Bray P-1 by a modified procedure of Laverty (37).

Exchangeable K was determined by reacting 2g of soil with 10 ml of a 1N NH_4OAc extracting solution. The solution was filtered and K was determined on the filtrate with the Perkin-Elmer Model No. 146 flame photometer. This is a modification of the procedure described by Jackson (32).

Calcium and Mg were determined by reacting 1g of soil with 25 ml of a 0.1N HCl extracting solution. The solution was filtered and Ca and Mg determined on the filtrate with the Jarrel-Ash atomic adsorption Model No. 82-156.

Soil pH was determined on a 1:1 soil solution ratio with a glass electrode on a Beckman pH meter.

Soluble salts were analyzed by filtering the 1:1 soil solution used in the pH determination and measuring electrical conductivity of the

filtrate with a solu bridge. Soil samples with electrical conductivities over 1.8 mmhos/cm were reanalyzed for salts with the saturated paste procedure (57).

Sodium was determined on the filtrate of the saturated paste with the flame photometer.

Three soil extraction methods were used to determine Zn. They were as follows:

1. A modified procedure of Nelson, Boawn, and Viets (43) which consisted of extracting 1g of soil with 25 ml of 0.1N HCl. The soil suspension was allowed to stand overnight before shaking for one-half hour. Zinc was determined on a clear filtrate with a Jarrel-Ash atomic absorption Model 82-156.
2. The $(NH_4)_2CO_3$-EDTA extraction procedure of Trierweiler and Lindsay (55).
3. The DTPA-TEA extraction procedure of Lindsay and Norvell (38).

Three soil extraction methods were used for S. They were as follows:

1. A $CaCl_2$ extraction procedure (Soils Department, University of Wisconsin, unpublished data).
2. A $Ca(H_2PO_4)_2$-HOAc extraction procedure (31).
3. A $Ca(H_2PO_4)_2$ extraction procedure (Munter, Rehm, Seim, and Grava, Soil Testing Laboratory, University of Minnesota, unpublished data).

Plant Analysis

Plant samples were dried at 65 C and ground with a Wiley mill. One gram sample of oven-dried plant material was digested with 10 ml of concentrated HNO_3 until the volume was reduced to 1-2 ml. The digest was allowed to cool and 2.5 ml of 70 percent perchloric acid was added and digestion continued. Digestion was completed after about 15 minutes or when there was 1-2 ml of clear solution remaining. After cooling, redistilled water was added to the flasks and the digest was filtered and brought to volume in 50 ml volumetric flasks (final dilution 1:50). This digestion procedure was a modification of the procedure outlined by Allan (1). Determinations for P, K, S, Ca, Mg, Fe, Zn, and Mn were made from this solution.

Calcium and Mg were determined by taking 0.1 ml of digestion solution, adding 10 ml of 150 ppm Sr solution (final dilution 1:5000), and analyzing by atomic absorption spectrophotometry.

The original 1:50 digestion solution was used directly to determine Fe, Mn, and Zn on the atomic absorption spectrophotometer.

Plant P was determined by taking 2 ml of plant digest, adding 43 ml of distilled water, and 5 ml of Barton's reagent (5). After 10 minutes the optical density of the yellow color was read on a Coleman-Junior spectrophotometer at 430 mμ.

Potassium was determined with the flame photometer on a solution consisting of a 1:1250 final dilution.

Plant S was determined by taking 5 ml of digestion solution, adding 5 ml of a buffer solution; which consisted of 40g $MgCl_2 \cdot 6H_2O$, 4.1g

NaOAc, 0.83g KNO_3, and 28 ml of 95 percent ethanol per liter, and diluting with 15 ml of distilled water. One scoop (about 0.4g) of $BaCl_2$ crystals was added and the solution was stirred for exactly one minute. Sulfur was determined by reading optical density at 420 mμ on the Coleman-Junior spectrophotometer.

Statistical Analysis

The experimental design was a 2x2x4x7 factorial which consisted of two levels of S, two levels of Zn, four non-adjacent replicates per location, and seven locations. The experiment was arranged in a randomized block design.

The analysis of variance was determined by computer with the aid of the station statistician, Dr. Lee Tucker.

Multiple regression analyses were conducted for Zn and S soil tests in conjunction with Zn and S plant concentration. This was done by computer with a stepwise multiple regression program and the aid of the station statistician.

The methods of Steel and Torrie (52) were used in the statistical analysis of the data.

RESULTS AND DISCUSSION

A field study with corn was established at several locations in order to determine which Zn soil test and which S soil test would compare most favorably with plant response as measured by plant Zn and S concentration and corn yields.

Plot Descriptions and Field Observations

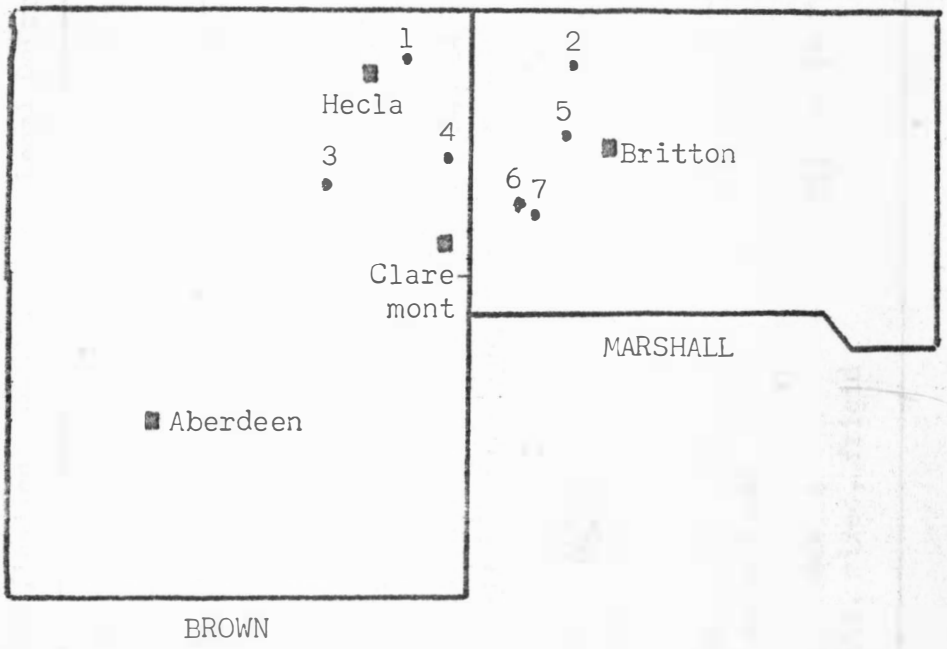
A field experiment was established in northern Brown and Marshall Counties. Figure 1 shows the location of each plot area. The general location of the field experiment was established on the basis of a preliminary study carried out in this area in the summer of 1970 (60).

Since the majority of the soils in the preliminary study were sandy, six of the seven locations in this study were also established on sandy soils. The Zuehlke location was a clay loam soil.

Table 2 lists the legal description and soil classification of all seven locations. A range of soils was selected in order to determine differences in S and Zn concentrations of plants and soils. Yield response was measured from additions of Zn and S to aid in the evaluation of the soil and plant analyses.

The Finley location had not received sufficient N and was extremely weedy at the time of the second plant sampling. Therefore, a N rate of 112 kg/ha was added after the plot was hand weeded. However, by this time the corn was suffering from an extreme N deficiency characterized by short, yellow appearing plants throughout the field.

Fig. 1. Location of seven field sites in Brown and Marshall Counties.



1. Finley location
2. Jarret location
3. Spurr location
4. Dinger location
5. Zuehlke location
6. Symmens location
7. Moeckley location

Table 2. Soil classification and field description of locations for the S and Zn study.

Cooperator	County	Soil Classification	Legal Description
Dinger	Brown	Pachic-Udic haploborolls coarse-loamy, mixed	SE$\frac{1}{4}$ sec 27 T127N R60W
Finley	Brown	Pachic-Udic haploborolls loamy, very fine sand, mixed	SE$\frac{1}{4}$ sec 19 T128N R60W
Jarret	Marshall	Pachic-Udic haploborolls sandy, mixed	S$\frac{1}{2}$ sec 21 T128N R58W
Moeckley	Marshall	Aeric calciaquolls coarse-loamy, mixed, frigid	SE$\frac{1}{4}$ sec 14 T126N R59W
Spurr	Brown	Pachic-Udic haploborolls loamy, very fine sand, mixed	SE$\frac{1}{4}$ sec 7 T126N R61W
Symmens	Marshall	Pachic-Udic haploborolls coarse-loamy, mixed	NW$\frac{1}{4}$ sec 15 T126N R59W
Zuehlke	Marshall	Aeric calciaquolls fine-silty, mixed, frigid	SE$\frac{1}{4}$ sec 19 T127N R58W

Table 3 shows plant N concentration at early and late sampling. There was a large drop in N concentration from the early to the late plant sampling date. The N levels for the corn fell far below the sufficiency levels of 2.76-3.50 percent outlined by Carson et al. (13).

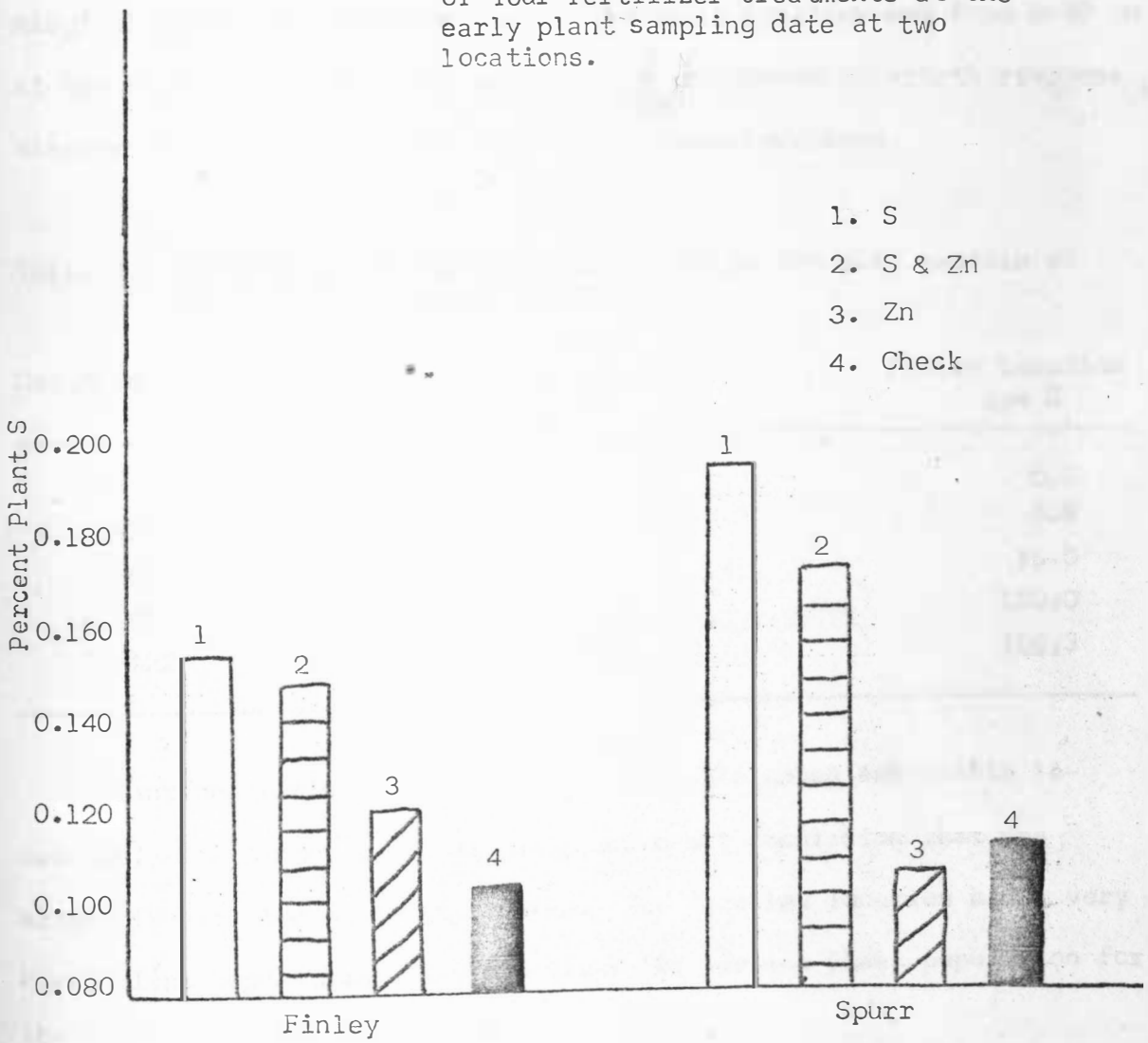
Table 3. Plant N concentration at the Finley location at early and late sampling dates.

Treatment	Percent N Early	Percent N Late
S	3.05	1.70
S & Zn	3.16	1.55
Zn	2.91	1.93
Check	3.27	1.91

Growth response to additional S was observed at the Finley and Spurr locations on June 23. Figure 2 is a photograph taken at the Finley location showing the growth response to S. This figure vividly illustrates the differences in plant height and color between corn receiving supplemental S and corn receiving no supplemental S. There were also large differences in plant S concentration at the Finley and Spurr locations on June 23 between the treatments receiving S and those receiving no S (Figure 3). Figures 2 and 3 demonstrate the response of corn at the early sampling date to additional S.

Fig. 2. Growth response to S at Finley location (early plant sampling).

Fig. 3. Average S concentrations of corn leaves of four fertilizer treatments at the early plant sampling date at two locations.



When the corn was in the silking stage the growth response attributed to S was less evident at both locations. This was expected at the Finley location since the N deficiency and weed problem had taken affect at this time. However, at the Spurr location apparently the corn plant roots extended down to a larger source of available S deeper in the soil profile (35). The average $Ca(H_2PO_4)_2$ - HOAc-extractable SO_4-S found in the profile at the Spurr and Finley locations is listed in Table 4. The SO_4-S levels were in the low to marginal range (31) from 0-61 cm at the Spurr location and from 0-30 cm at the Finley location which may explain the change in growth response observed from early to late sampling at these locations.

Table 4. $Ca(H_2PO_4)_2$ - HOAc-extractable SO_4-S in the soil profile at the Finley and Spurr locations.

Depth in Profile cm	Spurr Location ppm S	Finley Location ppm S
0-15	4.7	5.0
15-30	2.7	6.9
30-61	4.6	15.0
61-91	15.3	120.0
91-122	39.7	168.3

Plant populations were extremely variable among and within locations. The Jarret location had a low plant population that was extremely variable among replicates. The Moeckley location had a very heavy plant population. Table 5 lists the average plant population for the four treatments at each location.

Table 5. Average plant population for four fertilizer treatments at seven locations.

Treatments	Locations						
	Finley	Moeckley	Spurr	Zuehlke	Symmens	Dinger	Jarret
	Plants/ha						
S	32,794	57,097	38,749	34,068	36,827	52,204	23,949
S & Zn	30,778	57,203	40,498	35,766	36,615	51,262	23,142
Zn	29,186	59,538	38,076	34,917	37,039	52,070	24,084
Check	28,973	57,841	41,575	36,402	35,659	50,455	24,488

At the Dinger location, several Zn deficient corn plants were observed outside the plot area and within the plot area where no supplemental Zn was added. However, no growth response was observed in comparing Zn treated areas to areas receiving no Zn. Several Zn deficient plants were observed at the Spurr location and in some of the replicates it appeared that corn was responding to additional Zn.

Yield Data

The average yield per treatment at each location is listed in Table 6. No significant yield differences were obtained at any location (Appendix A). Yield differences between locations were highly significant which was not surprising since different weather conditions, management practices, etc. easily account for this variability.

Drought limited yields to some extent at all locations. This was evident by the wilted appearance of the corn later in the growing season and the large number of barren stalks found at harvest. More optimum soil moisture conditions may have resulted in a yield response to Zn and/or S.

At the Finley location, weedy conditions and lack of N as well as drought undoubtedly reduced yields and masked any possible yield response to S or Zn. At the Moeckley location there was a yield increase trend with the Zn treatments, however, this yield increase was non-significant.

Since no significant yield differences to additional Zn or S were obtained, plant analysis data were the criteria used to evaluate the various soil tests.

Table 6. Average corn yield for four treatments at seven locations.

Treatment	Location						
	Dinger	Finley	Jarrct	Moeckley	Spurr	Symmens	Zuehlke
	Corn Yield, kg/ha						
S	5308	3258	5971	5992	2294	3568	4754
S & Zn	4982	3037	5795	6650	2363	3172	5051
Zn	5813	3313	5887	6408	2173	3313	5390
Check	5490	3365	6203	6040	2284	3945	5101

Correlation Study

Stepwise multiple regression analyses were conducted for estimating plant Zn and S concentrations. In addition to the regression coefficients and coefficients of determination, simple correlation comparisons between all the variables entered were obtained. Some of the more important simple correlations are discussed.

SULFUR

The Literature Review covered some of the influences of organic matter on available soil S. From the data in Table 7 it appears that plant S correlated with organic matter only at the early sampling on the check plots. The correlation coefficients between soil organic matter and plant S concentrations for both late sampling treatments (S and no S) and the early sampling S treatment were quite low. Apparently the S treatment supplied enough additional S so the plants were not as dependent on organic matter as a source of available S. The late sampling correlations were low because the corn roots had extended down into greater sources of available inorganic S deeper in the soil profile.

A comparison of S soil tests at the 0-15 cm depth with organic matter gave the following correlation coefficients: 0.652** for organic matter x $Ca(H_2PO_4)_2$-HOAc, 0.284 for organic matter x $Ca(H_2PO_4)_2$, and 0.687** for organic matter x $CaCl_2$ (data not shown).

Table 7. Correlation coefficients of organic matter and plant N with plant S at two sampling dates with two S treatments.

Comparisons	Correlation Coefficients			
	Early Check	Late Check	Early S	Late S
Organic Matter x Plant S	0.550**	0.242	0.192	0.049
Plant N x Plant S	0.514**	0.587**	0.236	0.571**

**Significant at 0.01 level.

Table 7 also shows that plant N was significantly correlated with plant S on all but the early sampling S treatment plots. The N:S ratio in the soil as well as the role of both N and S in plant protein may have accounted for the significant correlation coefficients.

Simple correlation coefficients of the various soil tests with plant S revealed that $Ca(H_2PO_4)_2$-extractable S gave the highest correlation coefficient at the early sampling on the check plots (Table 8). There was a slight increase in the correlation coefficients of all soil tests with plant S on the early sampling check plots when soil sampling depth was increased to 61 cm.

Close examination of Table 8 revealed only small differences in correlation coefficients among all soil tests between the two treatments at late sampling. Correlation coefficients of the early

Table 8. Simple correlation coefficients for plant S at two sampling dates and two S treatments with three S soil tests at two soil depths.

Soil Test	Soil Sample Depth, cm	Correlation Coefficients: Early Check	Late Check	Early S	Late S
$Ca(H_2PO_4)_2$ - HOAc	0-15	0.478**	0.378*	0.199	0.364
$Ca(H_2PO_4)_2$	0-15	0.732**	0.590**	0.178	0.538**
$CaCl_2$	0-15	0.537**	0.277	0.134	0.232
$Ca(H_2PO_4)_2$ - HOAc	0-61	0.612**	0.631**	0.340	0.625**
$Ca(H_2PO_4)_2$	0-61	0.754**	0.548**	0.240	0.472*
$CaCl_2$	0-61	0.556**	0.286	0.238	0.277

*Significant at 0.05 level.
**Significant at 0.01 level.

sampling S treatments were quite low while the coefficients of the early sampling check plots were usually the highest. Apparently when S was applied or when plant samples were taken later in the growing season, soil S was not as much of a limiting factor as it was earlier in the season where no additional S was applied. Therefore, correlation coefficients between S soil tests and plant S tended to be lower at the late sampling.

The depth of soil sampling was an important consideration in determining the S status of a particular area. This was illustrated by the following field observations:

(a) growth response of corn to applied S early in the growing season.

(b) growth response was less apparent later in the growing season.

(c) no yield response was obtained.

These observations along with the organic matter x plant S comparison in Table 7 and the comparisons in Table 8 demonstrated the importance of finding a S test capable of extracting plant available S from the soil at greater depths as well as from the topsoil.

Comparisons of S soil tests with one another and their corresponding correlation coefficients are shown in Table 9. The $CaCl_2$ x $Ca(H_2PO_4)_2$ - HOAc comparisons had the highest correlation coefficient at 0-15 cm whereas at 0-61 cm the highest correlation coefficient was obtained with the $Ca(H_2PO_4)_2$ x $CaCl_2$ comparison. All of the comparisons were highly significant which indicated that the tests measured approximately the same amounts of soil S.

Table 9. Correlation coefficients of comparisons between S soil tests.

Comparison	Soil Sample cm	Correlation Coefficient
$Ca(H_2PO_4)_2$ x $Ca(H_2PO_4)_2$ - HOAc	0-15	0.598**
$Ca(H_2PO_4)_2$ - HOAc x $CaCl_2$	0-15	0.853**
$Ca(H_2PO_4)_2$ x $CaCl_2$	0-15	0.689**
$Ca(H_2PO_4)_2$ - HOAc x $Ca(H_2PO_4)_2$	0-61	0.805**
$Ca(H_2PO_4)_2$ - HOAc x $CaCl_2$	0-61	0.778**
$Ca(H_2PO_4)_2$ x $CaCl_2$	0-61	0.825**

**Significant at 0.01 level.

ZINC

Correlation coefficients of various Zn soil tests with plant Zn concentrations were very low (Table 10). The numerous negative r values were unusual compared to the findings of other workers (38, 43, 55).

Table 10. Simple correlation coefficients of plant Zn at two sampling dates and two Zn treatments with three Zn soil tests at two soil depths.

Soil Test	Soil Sample Depth, cm	Correlation Coefficients: Early Sampling Check	Late Sampling Check	Early Zn	Late Zn
DTPA	0-15	-0.062	-0.104	-0.362	-0.167
EDTA-$(NH_4)_2CO_3$	0-15	-0.086	-0.128	-0.328	-0.171
0.1N HCl	0-15	0.239	-0.103	0.364	-0.040
DTPA	0-61	0.174	0.188	0.299	0.185
EDTA-$(NH_4)_2CO_3$	0-61	0.188	0.129	0.366	0.195
0.1N HCl	0-61	0.092	-0.094	0.211	0.013

Deep sampling improved the correlation coefficients of plant Zn with DTPA and EDTA soil Zn but the improvements were not enough to give any significant r values.

Table 11 lists the correlation coefficients of comparisons between various Zn soil tests. All of the soil tests were significantly correlated with one another. Very high correlation coefficients of DTPA x EDTA were obtained at both soil depths. Apparently both of these chelating extractants complexed the same soil Zn fraction in almost the same amount (Table 12).

Table 11. Correlation coefficients of comparisons between Zn soil tests.

Comparison	Soil Sample Depth, cm	Correlation Coefficients
DTPA x EDTA	0-15	0.984**
DTPA x HCl	0-15	0.458*
EDTA x HCl	0-15	0.483**
DTPA x EDTA	0-61	0.839**
DTPA x HCl	0-61	0.534**
EDTA x HCl	0-61	0.504**

*Significant at 0.05 level.
**Significant at 0.01 level.

Table 12. Comparison of the amounts of Zn extracted by EDTA and DTPA.

	Soil Depth 0-15 cm		Soil Depth 0-61 cm	
Cooperator	EDTA ppm Zn	DTPA ppm Zn	EDTA ppm Zn	DTPA ppm Zn
Symmens	1.81	1.55	0.70	0.68
Moeckley	1.52	1.19	0.79	0.75
Jarret	1.44	1.29	0.51	0.48
Zuehlke	1.12	0.90	0.63	0.68
Dinger	1.14	0.90	0.76	0.70
Spurr	2.24	2.03	0.71	0.69
Finley	1.22	0.99	0.47	0.41

Correlation coefficients were greater for the DTPA x HCl and EDTA x HCl comparisons at the 0-61 cm soil depth than at the 0-15 cm depth (Table 11).

Multiple Regression

Stepwise multiple regression programs were used to determine which variables significantly affected plant S and Zn concentrations (dependent variables). A total of 15 independent variables for Zn and 13 independent variables for S were studied. The independent variables are numbered and described in Table 13 for S and Table 14 for Zn. The process of selection of the various independent variables entered in the regression analyses for Zn and S was based on the importance that these variables were thought to have on plant Zn and/or S concentration.

Multiple Regression Analyses of S

Table 15 lists the standardized regression coefficients, intercepts, R^2 values, and significant variables of the regression equations for S (see Appendixes B-E for order of entry and standard partial regression coefficients of complete equations). A significant reduction in sum of squares attributed to regression occurred when seven of the 12 independent variables were included in equation Y_1. The coefficient of determination (R^2) was 0.898 which means that seven of the 12 independent variables explained 89.8 percent of the variability in plant S. Although the R^2 value indicated that the equation adequately predicted plant S, it was considered impractical to use all seven of these variables.

Table 13. Description of independent variables used in the regression analysis for S (dependent variable was percent plant S).

Independent Variable (X)	Variable Description
2	$Ca(H_2PO_4)_2$-HOAc-extractable S, ppm, 0-15 cm
3	$Ca(H_2PO_4)_2$-extractable S, ppm, 0-15 cm
4	$CaCl_2$-extractable S, ppm, 0-15 cm
5	$Ca(H_2PO_4)_2$-HOAc-extractable S, ppm, 0-61 cm
6	$Ca(H_2PO_4)_2$-extractable S, ppm, 0-61 cm
7	$CaCl_2$-extractable S, ppm, 0-61 cm
8	Percent soil organic matter
9	P in soil kg P/ha
10	Soil pH
11	Soluble salts in soil
12	Percent N in plant
13	ppm Zn in plant
*14	Percent S in plant early sampling

*Variable entered only when plant S late sampling was dependent variable.

Table 14. Description of independent variables used in the regression analysis for Zn (Dependent variable was ppm plant Zn).

Independent Variable (X)	Variable Description
2	DTPA-extractable Zn, ppm, 0-15 cm
3	EDTA$(NH_4)_2CO_3$-extractable Zn, ppm, 0-15 cm
4	0.1N HCl-extractable Zn, ppm, 0-15 cm
5	DTPA-extractable Zn, ppm, 0-61 cm
6	EDTA$(NH_2)_4CO_3$-extractable Zn, ppm, 0-61 cm
7	0.1N HCl-extractable Zn, ppm, 0-61 cm
8	Percent soil organic matter
9	Soil pH
10	Ca & Mg, 0-15 cm, meq/100g of soil
11	P in soil kg/ha
12	Percent N in plant
13	Percent P in plant
14	Percent K in plant
15	Percent S in plant
*16	Plant Zn early sampling (ppm)

*Variable entered only when plant Zn late sampling was the dependent variable.

Table 15. The intercepts, variables, regression coefficients, standardized regression coefficients, and R^2 values of significant equations for plant S at two sampling dates with two S treatments.

Sampling Date and Treatment	Intercept	Independent Variable	Regression Coefficient	Standardized Regression Coefficients	R^2
Early Check (Y_1)	0.101	X_6	0.002	1.017	
		X_8	0.053	0.766	
		X_7	-0.0004	-0.615	
		X_4	-0.0006	-0.340	
		X_9	-0.001	-0.325	
		X_{12}	0.039	0.260	
		X_{10}	-0.025	-0.263	0.898
Late Check (Y_2)	-0.152	X_{14}	0.655	1.135	
		X_{10}	0.027	0.489	
		X_8	-0.024	-0.600	
		X_5	0.0002	0.357	
		X_7	0.0002	0.639	
		X_{12}	0.001	0.018	
		X_2	-0.0001	-0.134	
		X_{11}	-0.0002	-0.002	
		X_9	0.0002	0.151	
		X_6	-0.002	-2.109	
		X_3	0.003	1.333	0.913
Early S (Y_3)	0.567	X_5	0.0002	0.274	
		X_{13}	0.007	0.689	
		X_{10}	-0.062	-0.746	
		X_9	-0.001	-0.483	0.440
Late S (Y_4)	0.215	X_5	0.0007	1.033	
		X_{12}	0.048	0.729	
		X_8	-0.007	-0.156	
		X_{10}	-0.029	0.480	
		X_7	-0.0002	-0.483	0.860

However, the first two variables entered in equation Y_1 explained 66.0 percent of the S concentration variation (Table 16). These variables were X_6($Ca(H_2PO_4)_2$-extractable S) and X_8(soil organic matter). The equation for these two variables was as follows:

$$Y_5 = 0.082 + 0.00099\,X_6 + 0.023\,X_8$$

where Y_5 = percent S in the plant, X_6 = $Ca(H_2PO_4)_2$-extractable S, and X_8 = soil organic matter. Development of this equation for practical use was more feasible since it involved only two easily measured variables.

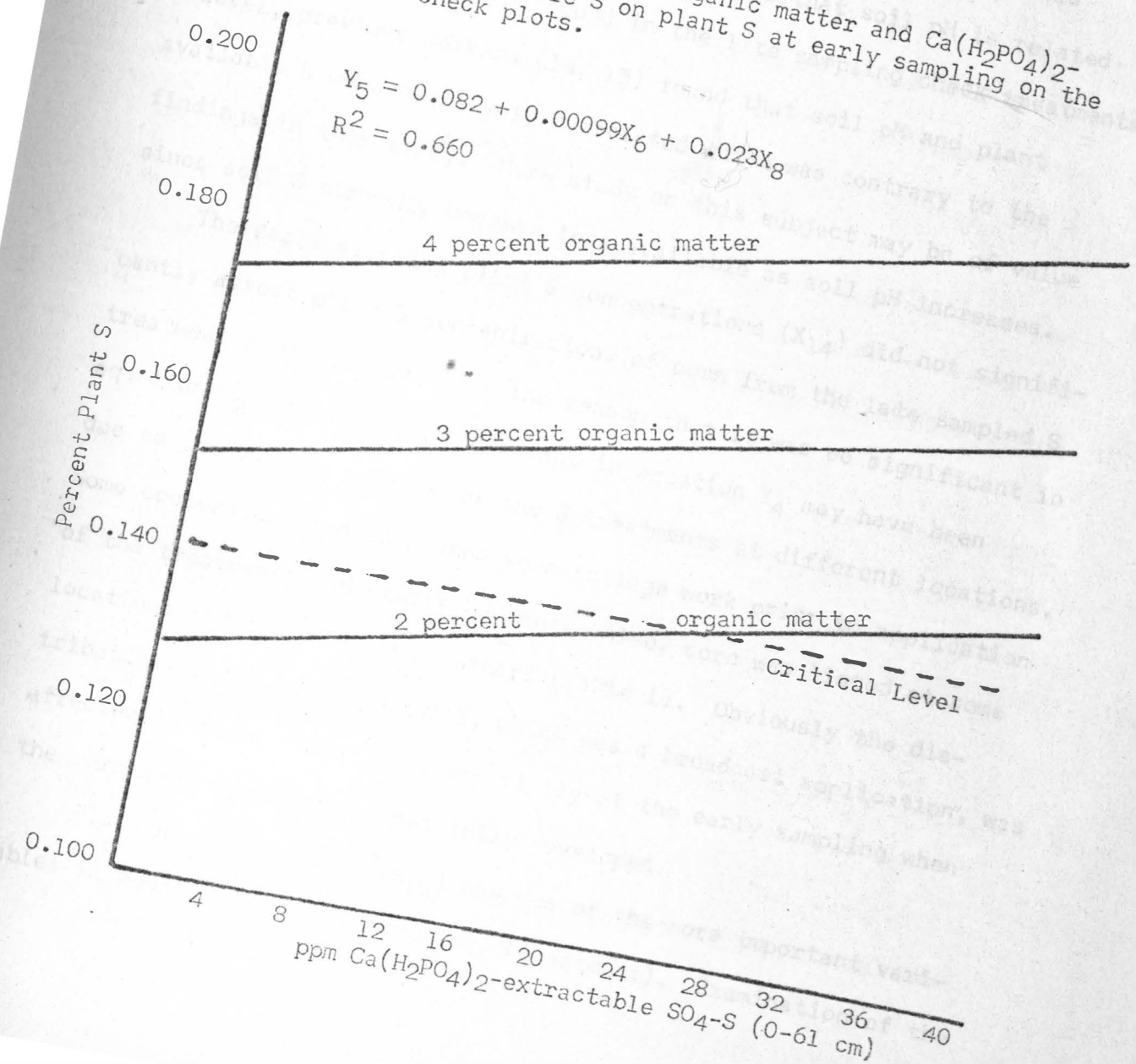
Several regression lines developed from equation Y_5 are illustrated in Fig. 4. It was evident that as both organic matter and $Ca(H_2PO_4)_2$-extractable SO_4-S test values increased, there were corresponding increases in plant S. The simple correlation of organic matter X plant S illustrated in Table 7 as well as the relationship shown in Fig. 4 reveal that organic matter was of some importance in predicting plant S at the early sampling dates on the check treatments.

A critical level for plant S has not been definitely established in the literature. A level of 0.140 percent has been the accepted value from work carried out by the soil testing laboratory at South Dakota State University (R. C. Ward and P. L. Carson, personal communication). On the basis of this critical level and upon examination of Fig. 4, it appeared that as organic matter approached 3 percent regardless of the soil test value obtained with $Ca(H_2PO_4)_2$, the level of plant S was sufficient.

Table 16. The R^2 values and variables entered at each step of the regression analysis up to and including the last step of significance.

	Sampling Date and Treatment							
	Early Check		Late Check		Early S		Late S	
Step Number	R^2	Variable Entered	R^2	Variable Entered	R^2	Variable Entered	R^2	Variable Entered
1	0.568	X_6	0.604	X_{14}	0.115	X_5	0.391	X_5
2	0.660	X_8	0.703	X_{10}	0.190	X_{13}	0.589	X_{12}
3	0.780	X_7	0.818	X_8	0.312	X_{10}	0.731	X_8
4	0.823	X_4	0.836	X_5	0.440	X_9	0.810	X_{10}
5	0.855	X_9	0.865	X_7			0.860	X_7
6	0.867	X_{12}	0.875	X_{12}				
7	0.898	X_{10}	0.878	X_2				
8			0.881	X_{11}				
9			0.884	X_9				
10			0.885	X_6				
11			0.913	X_3				

Fig. 4. The influence of organic matter and $Ca(H_2PO_4)_2$-extractable S on plant S at early sampling on the check plots.



The early sampling plant S concentrations (X_{14}) were highly significant in predicting plant S concentrations in the late sampled check plots. The R^2 value was 0.604 (Table 16). The addition of organic matter (X_8) and soil pH (X_{10}) increased the R^2 value to 0.818.

The simple correlations of soil pH with plant S ($r = 0.468^*$) in addition to the increase in the R^2 value when soil pH (X_{10}) was entered as a variable (Table 16) indicates that soil pH is related to plant S concentrations found in the late sampling check treatments. However, previous workers (14, 15) found that soil pH and plant available S were negatively correlated which was contrary to the findings in this study. More study on this subject may be of value since soil S commonly becomes less available as soil pH increases.

The early sampling plant S concentrations (X_{14}) did not significantly affect plant S concentrations of corn from the late sampled S treatment plots (Table 15). The reason that it was so significant in equation Y_2 and was not significant in equation Y_4 may have been due to the varying effects of the S treatments at different locations. Some cooperators had conducted some tillage work prior to application of the treatments and others had not. Also, corn was listed at some locations and top-planted at others (Table 1). Obviously the distribution of the supplemental S, which was a broadcast application, was affected in these situations, especially at the early sampling when the corn root systems were not fully developed.

Plant N concentration (X_{12}) was one of the more important variables in equation Y_4 (late sampling, S treatment). Examination of the

R^2 values for equation Y_4 (Table 16) revealed an increased R^2 value from 0.391 to 0.589 when plant N (X_{12}) was entered as a variable. The relationship of plant N (X_{12}) and $Ca(H_2PO_4)_2$-HOAc-extractable S (X_{15}) on plant S concentration is shown in Fig. 5. Figure 5 illustrates the importance of plant N to plant S concentration.

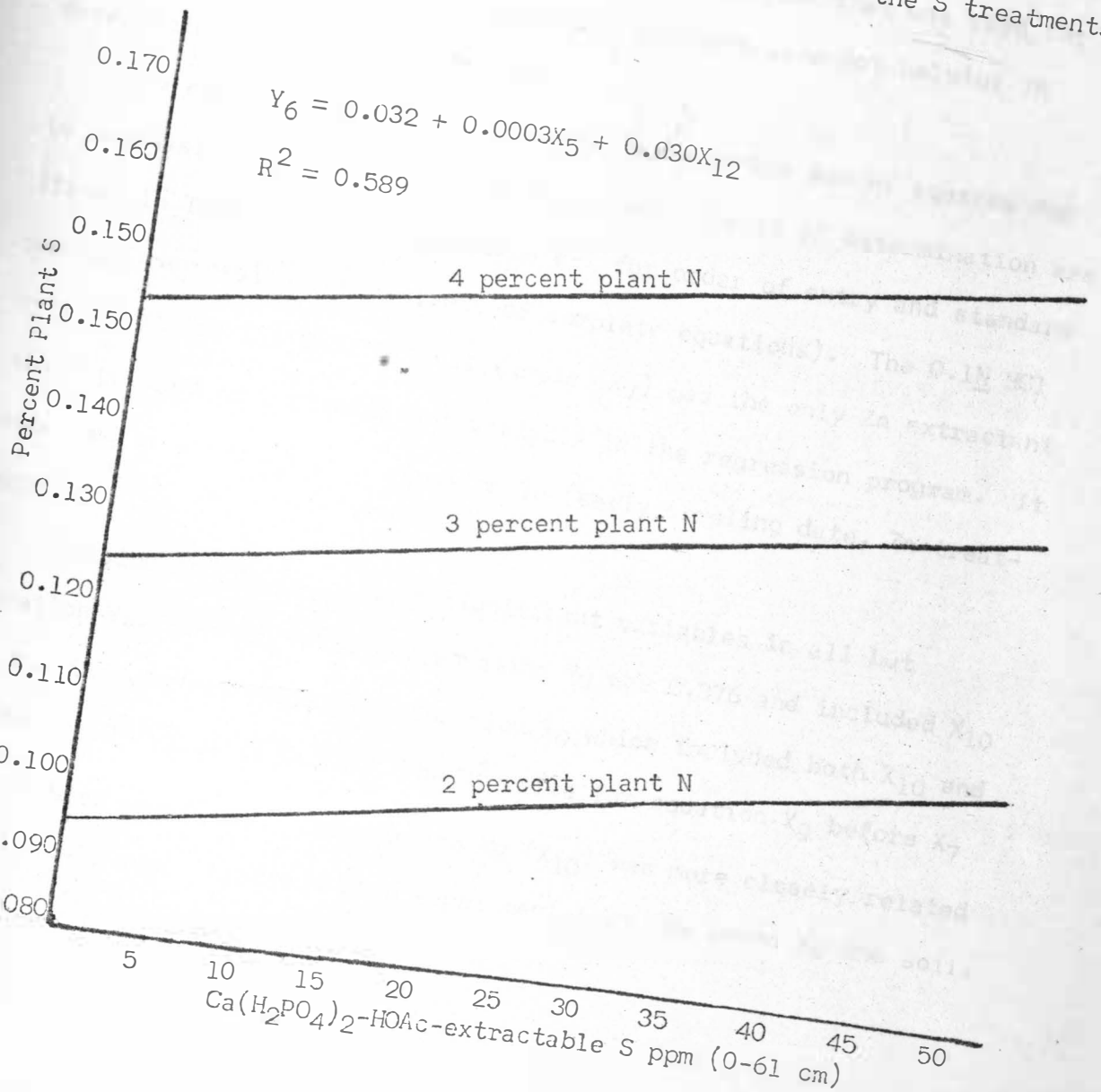
In the literature N:S ratio was demonstrated to be an effective means of determining the S status of plants (28, 44). It appears that this may be just as important in evaluating plant S status as establishing a critical plant S level. Certainly more work needs to be carried out in the plant analysis area to determine critical plant S levels or N:S ratios.

The $Ca(H_2PO_4)_2$-HOAc extractant (X_5) was an important variable in explaining plant S variation on the S treatments at both sampling dates (Table 15). It was also entered as the fourth variable on the late sampling check plots (Table 16).

The $Ca(H_2PO_4)_2$ extractant (X_6) was the first variable entered in equation Y_1 (Table 15), whereas $Ca(H_2PO_4)_2$-HOAc was not entered as a significant variable in this equation. Both extractants (X_5 and X_6) measured soil S at 0-61 cm in the profile which demonstrated the importance of taking deeper soil samples to make soil S determinations.

Evaluation of the various S soil tests indicated either $Ca(H_2PO_4)_2$-HOAc or $Ca(H_2PO_4)$ as most reliable for predicting plant S. However, the drought factor, the lack of growth response observations noted at the late sampling date, and the added S for the S treatments

Fig. 5. Influence of plant N and $Ca(H_2PO_4)_2$-HOAc-extractable SO_4-S on plant S at late sampling on the S treatments.



may have affected the variation in plant S in some inexplainable way. The $Ca(H_2PO_4)_2$ extractant for the 0-61 cm profile was considered more reliable in predicting plant S since it was the first variable entered in the regression analysis for the early sampled check plots.

Multiple Regression Analyses of Zn

The same stepwise multiple regression program that was used for S was also used for Zn. The regression analyses were not helpful in determining the best soil Zn test.

The equations which significantly reduced the sum of squares due to regression and their corresponding coefficients of determination are listed in Table 17 (see Appendixes F-I for order of entry and standard partial regression coefficients of complete equations). The 0.1N HCl extractant for the 0-61 cm soil sample (X_7) was the only Zn extractant that appeared as a significant variable in the regression program. It appeared as a variable in equation Y_9 (early sampling date, Zn treatment).

Calcium and Mg (X_{10}) were significant variables in all but equation Y_8. The R^2 value for equation Y_7 was 0.376 and included X_{10} as the independent variable. Equation Y_9 which included both X_{10} and X_7 had an R^2 value of 0.678. The R^2 value for equation Y_9 before X_7 was entered was 0.529. Calcium and Mg (X_{10}) was more closely related to plant Zn concentrations when supplemental Zn was added to the soil.

Table 17. Significant variables of regression equations at two sampling dates with two Zn treatments.

	Early Sampling Check (Y_7)	Late Sampling Check (Y_8)	Early Sampling Zn (Y_9)	Late Sampling Zn (Y_{10})
Intercept	14.59	8.66	2.50	6.65
Variables	$0.08X_{10}$	$70.60X_{15}$	$0.15X_{10}$	$92.26X_{15}$
			$2.73X_7$	$0.07X_{10}$
R^2	0.376	0.248	0.678	0.632

Plant S (X_{15}) was significantly related to plant Zn concentration at the late sampling date on both Zn treatments (Table 17). Figure 6 is a graph of equation Y_8 showing the relationship of plant S (X_{15}) to plant Zn concentration. The equation for Y_{10} (Fig. 7) demonstrates the effect of both plant S (X_{15}) and soil Ca and Mg (X_{10}) on plant Zn concentrations.

Sauchelli (47) proposed that the presence of ions such as NO_3^{-1}, SO_4^{-2}, or Cl^{-1} favor the formation of soluble Zn compounds, hence the availability of Zn increases. Therefore, an increase in plant SO_4-S indicates an increased source of soil SO_4-S which in turn might make soil Zn more available to plants resulting in increased concentration of plant Zn. This may explain why plant S affected plant Zn concentration only at the late sampling. Growth response to additional S was not evident later in the growing season, indicating that corn had picked up additional SO_4-S in the soil. Based on Sauchelli's (47) proposal, this additional SO_4-S may have increased the formation of soluble Zn compounds and hence caused an increase in plant Zn concentration. However, no conclusive evidence from this study was found to support such a proposal. Equations Y_8 and Y_{10} in Table 17 indicate that a more detailed study of the mutual effects of plant S and Zn upon one another needs to be conducted. A study such as this might

Fig. 6. The influence of plant S on plant Zn concentration (late sampling, check).

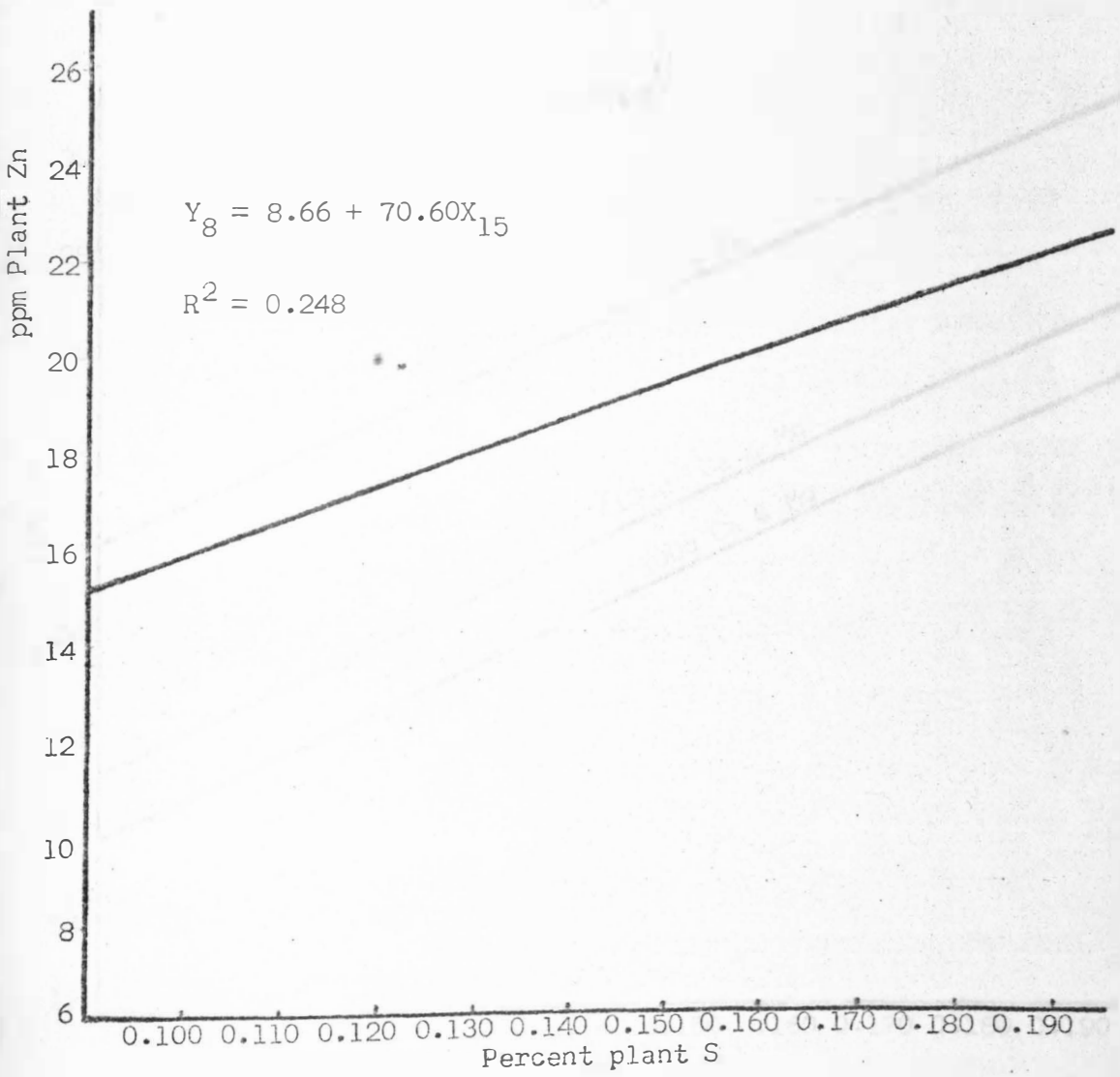
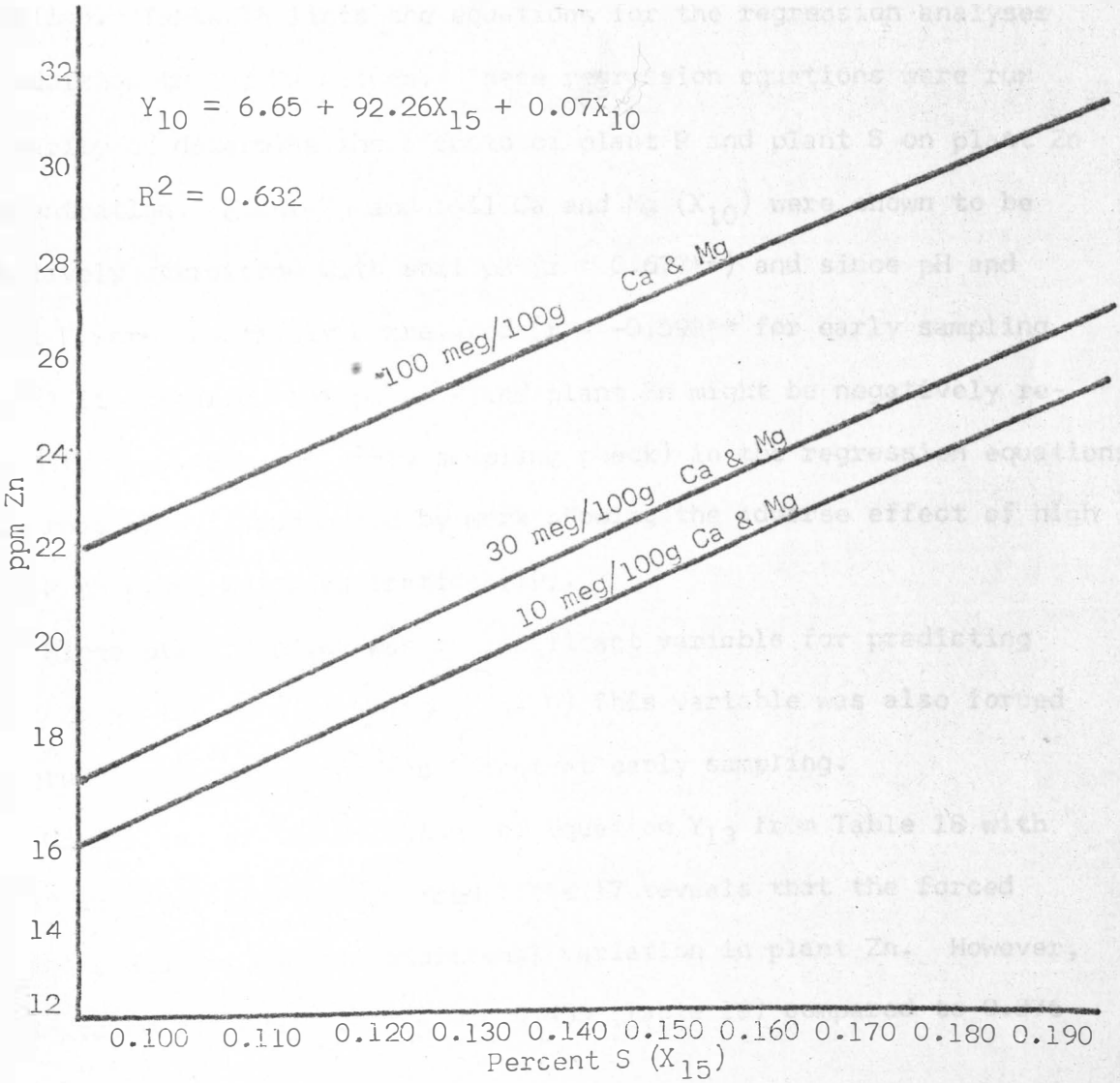


Fig. 7. The influence of plant S (X_{15}) and soil Ca and Mg (X_{10}) on the concentration of plant Zn (late sampling, Zn).



reveal the importance of simultaneously evaluating plant S and Zn when an apparent deficiency of one or the other occurs.

Other stepwise multiple regression equations were developed for the early plant sampling dates for both the applied Zn and check treatments. Three variables were forced in each case. Plant P (X_{13}), plant S (X_{15}), and 0.1N HCl-extractable Zn in a 0-61 cm profile (X_7) were forced for the early sampling while plant S, plant P, and DTPA-extractable Zn in a 0-15 cm profile (X_2) were forced for the late sampling. Table 18 lists the equations for the regression analyses in addition to the R^2 values. These regression equations were run primarily to determine the effects of plant P and plant S on plant Zn concentration. Plant Zn and soil Ca and Mg (X_{10}) were shown to be positively correlated with soil pH ($r = 0.677^{**}$) and since pH and plant P were negatively correlated ($r = -0.598^{**}$ for early sampling check) it appeared that plant P and plant Zn might be negatively related ($r = -0.420^{*}$ for early sampling check) in the regression equations. This reasoning is supported by work showing the adverse effect of high soil P on plant Zn concentration (19).

Since plant S (X_{15}) was a significant variable for predicting plant Zn at the late sampling (Fig. 6) this variable was also forced to more closely determine its effect at early sampling.

Comparison of the R^2 values of equation Y_{13} from Table 18 with the R^2 value of equation Y_9 from Table 17 reveals that the forced variables did not explain additional variation in plant Zn. However, the R^2 value for equation Y_{15} was 0.435 (Table 18) compared to 0.376

Table 18. Significant equations and corresponding coefficients of determination for stepwise multiple regression program with three variables forced.

	Equation	R^2
*Step 1-3 for Zn early sampling	$Y_{12} = 34.00 - 44.32X_{13} + 1.52X_7 - 18.92X_{15}$	0.253
Step 1-4 for Zn early sampling	$Y_{13} = 3.36 + 1.43X_{13} + 2.71X_7 - 9.62X_{15} + 0.15X_{10}$	0.682
*Step 1-3 for check early sampling	$Y_{14} = 28.82 = 25.86X_{13} - 3.70X_{15} - 0.25X_2$	0.178
Step 1-4 for check early sampling	$Y_{15} = 7.96 + 3.20X_{13} + 3.60X_{15} + 3.14X_2 + 0.09X_{10}$	0.435
Step 1 for check early sampling	$Y_{16} = 27.68 - 25.18X_{13}$	0.177

*Three variables forced in the order that they appear in the equations.

for equation Y_7 (Table 17). This indicates that the introduction of the forced variables helped explain more variation in plant Zn at the early sampling on the check treatments.

A comparison of equation Y_{14} with Y_{16} reveals that plant P (X_{13}) was most important of the forced variables since it alone gave an R^2 value of 0.177 while the inclusion of X_{15} and X_{12} in the equation increased the R^2 value from 0.177 to 0.178.

Calcium and Mg (X_{10}) alone influenced the variation in plant Zn more than the following variables together: plant S (X_{15}), plant P (X_{13}), and soil Zn test X_2 or X_7.

The stepwise multiple regression analyses for Zn did not designate any soil test as being particularly effective in predicting the Zn status of corn plants.

SUMMARY AND CONCLUSIONS

The objectives of this study were: (a) to find a S soil test for predicting S concentration in corn plants, (b) to find a Zn soil test for predicting Zn concentration in corn plants, and (c) to determine corn yield response to additions of S and Zn.

No significant yield differences were found for corn grown on plots with Zn and/or S compared to the check plots. Although a growth response to S appeared early in the growing season at the Finley and Spurr locations, it was much less evident later in the season. It was concluded that the corn roots extended down into the soil profile to an additional source of available soil S later in the season.

Plant S and plant Zn were used as dependent variables in separate stepwise multiple regression analyses. Simple correlation coefficients were also obtained from this program.

Soil organic matter was found to be significantly correlated with plant S at the early sampling date on the check treatments ($r = 0.550^{**}$). The importance of soil organic matter was also evident from the following practical and significant ($R^2 = 0.660^{*}$) equation:

$$Y_5 = 0.082 + 0.00099\,X_6 + 0.023\,X_8$$

where Y_5 = percent S in corn plants for the early sampled check plots, $X_6 = Ca(H_2PO_4)_2$-extractable S 0-61 cm, ppm; and X_8 = soil organic matter, percent. Development of equation Y_5 into regression lines at different soil organic matter levels showed that as soil organic matter

approached 3 percent, there was little need of supplemental S regardless of the $Ca(H_2PO_4)_2$ soil test value. From the above information it was concluded that soil organic matter was very important as a source of available S early in the season before the corn roots reached an additional S supply deeper in the profile and where no additional S had been applied.

Simple correlation coefficients of plant N x plant S were significant on all but the early sampled S treatments. In addition, plant N appeared as one of the more important significant variables of the late sampled S plots where it along with $Ca(H_2PO_4)_2$-HOAc-extractable S for the 0-61 cm depth accounted for 58.9 percent of the variation in plant S. It was concluded that more work was needed to establish whether a plant N:S ratio or a critical plant S level was more important in establishing the S status of plants.

Depth of soil sampling improved the correlation coefficients of the S soil extractants in all cases on the early sampled check plots. The regression analyses for both sampling dates of the S treatments had $Ca(H_2PO_4)_2$-HOAc 0-61 cm as the first variable entered in the program while $Ca(H_2PO_4)_2$ 0-61 cm was the first variable entered for the early sampled check treatment analysis. Soil sampling depth was obviously important when considering the above results in addition to the observations of plant growth response made during the season.

No single S soil test was the best in predicting variation in plant S over all treatments and sampling dates. The $Ca(H_2PO_4)_2$-HOAc 0-61 cm

extractant was the first variable entered in the regression equations for early and late sampling of the S treatments. However the R^2 values were only 0.115 and 0.391, respectively. For the early sampled check treatment $Ca(H_2PO_4)_2$ 0-61 cm accounted for 56.8 percent of the variation in plant S.

The $Ca(H_2PO_4)_2$-extractable S in the 0-61 cm profile was considered the best S extractant based on its higher R^2 value on the early sampled check plots. Equation Y_5 which included $Ca(H_2PO_4)$ 0-61 cm as well as organic matter as variables was considered the best equation ($R^2 = 0.660$) that could be practically developed for estimating plant S and therefore might be useful in determining the S status of South Dakota soils.

The correlation coefficients of plant Zn with any of the three soil Zn extractants were very low. However, the correlation coefficients between the various soil Zn extractants were quite high, particularly the DTPA x EDTA comparison ($r = 0.984^{**}$). It was concluded that DTPA and EDTA measured the same soil Zn fraction in nearly equal amounts.

Soil Ca and Mg(X_{10}) was a very important variable in the regression analysis for predicting Zn concentration in corn plants, especially for the Zn treated plots.

Plant S was found to be a significant variable in predicting the variation in plant Zn at late sampling for both Zn treatments. However, more study on the mutual effects of plant S and plant Zn on one another needs to be conducted before any conclusions can be drawn.

Additional regression analyses were carried out with several independent variables forced into the program. Two of the forced variables of particular interest were plant S and plant P. Only at the early sampling check plot did the forced variables appear to increase the R^2 value. Most of the increase in the R^2 value was due to plant P, however, the increase was not very great in comparison with the variation in plant Zn attributed to Ca and Mg.

The correlation and regression analyses indicated that none of the soil Zn tests adequately predicted variation in plant Zn concentration.

I feel that a study similar to that conducted in the summer of 1970 on a more extensive basis would prove to be more fruitful in differentiating between various soil S and Zn extractants. If soil samples and plant samples were taken during the growing season from deficient and non-deficient appearing areas and compared, I am sure more conclusive evidence favoring a particular soil test for Zn and a particular soil test for S would result.

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Appendix A. Analysis of Variance of Yield Data with Different S and Zn Treatments at the Seven Field Sites.

Source of Variation	df.	Mean Squares	F-test
Zinc (Z)	1	1.24	0.003 ns
Sulfur (S)	1	155.57	1.43 ns
Z x S	1	0.03	0.001 ns
R	3	263.47	
Z x R	3	375.01	
S x R	3	109.03	
Z x S x R	6	23.31	
Cooperator (C)	6	6314.44	7.13 **
Z x C	6	78.32	0.81 ns
S x C	6	33.39	0.17 ns
Z x S x C	6	18.11	0.26 ns
RC	18	885.89	
Z x R x C	18	96.42	
S x R x C	18	197.08	
Z x S x R x C	18	70.33	

ns non-significant.

** F-test significant at 0.01 level.

Appendix B. Standard Partial Regression Coefficients of All Variables Entered in Last Step of S Analysis (Early Sampling, Check Treatment).

Variable	Standardized Regression Coefficients
X_6, $Ca(H_2PO_4)_2$-extractable S ppm (0-61 cm)	2.054
X_8, Percent soil organic matter	0.847
X_7, $CaCl_2$-extractable S ppm (0-61 cm)	1.154
X_4, $CaCl_2$-extractable S ppm (0-15 cm)	0.299
X_9, Soil P kg/ha	0.309
X_{12}, Percent N in plant	0.282
X_{10}, Soil pH	0.340
X_3, $Ca(H_2PO_4)_2$-extractable S ppm (0-15 cm)	0.850
X_2, $Ca(H_2PO_4)_2$-HOAc-extractable S ppm (0-15 cm)	0.297
X_{13}, ppm Zn in plant	0.049
X_{11}, Soluble salts	0.084
X_5, $Ca(H_2PO_4)_2$-HOAc-extractable S ppm (0-61 cm)	0.000

Appendix C. Standard Partial Regression Coefficients of All Variables Entered in Last Step of S Analysis (Late Sampling, Check Treatment).

Variable	Standardized Regression Coefficients
X_{14}, Percent S in plant at early sampling	1.135
X_{10}, Soil pH	0.497
X_8, Percent soil organic matter	0.617
X_5, $Ca(H_2PO_4)_2$-HOAc-extractable S ppm (0-61 cm)	0.391
X_7, $CaCl_2$-extractable S ppm (0-61 cm)	0.665
X_{12}, Percent N in plant	0.027
X_2, $Ca(H_2PO_4)_2$-HOAc-extractable S ppm (0-15 cm)	0.206
X_{11}, Soluble salts	0.048
X_9, Soil P kg/ha	0.145
X_6, $Ca(H_2PO_4)_2$-extractable S ppm (0-61 cm)	2.120
X_3, $Ca(H_2PO_4)_2$-extractable S ppm (0-15 cm)	1.310
X_4, $CaCl_2$-extractable S ppm (0-15 cm)	0.132
X_{13}, ppm Zn in plant	0.014

Appendix D. Standard Partial Regression Coefficients of All Variables Entered in Last Step of S Analysis (Early Sampling, S Treatment).

Variables	Standardized Regression Coefficients
X_5, $Ca(H_2PO_4)_2$-HOAc-extractable S ppm (0-61 cm)	1.107
X_{13}, ppm Zn in plant	0.704
X_{10}, Soil pH	0.978
X_9, Soil P kg/ha	0.538
X_3, $Ca(H_2PO_4)_2$-extractable S ppm (0-15 cm)	1.387
X_8, Percent soil organic matter	0.230
X_{12}, Percent N in plant	0.271
X_4, $CaCl_2$-extractable S ppm (0-15 cm)	1.388
X_2, $Ca(H_2PO_4)_2$-HOAc-extractable S ppm (0-15 cm)	0.752
X_{11}, Soluble salts	0.466
X_7, $CaCl_2$-extractable S ppm (0-61 cm)	0.411
X_6, $Ca(H_2PO_4)_2$-extractable S ppm (0-61 cm)	0.474

Appendix E. Standard Partial Regression Coefficients of All Variables Entered in Last Step of S Analysis (Late Sampling, S Treatment).

Variable	Standardized Regression Coefficients
X_5, $Ca(H_2PO_4)_2$-HOAc-extractable S ppm (0-61 cm)	1.245
X_{12}, Percent N in plant	0.718
X_8, Percent soil organic matter	0.339
X_{10}, Soil pH	0.385
X_7, $CaCl_2$-extractable S ppm (0-61 cm)	0.072
X_{11}, Soluble salts	0.271
X_{13}, ppm plant Zn	0.044
X_6, $Ca(H_2PO_4)_2$-extractable S ppm (0-61 cm)	1.119
X_3, $Ca(H_2PO_4)_2$-extractable S ppm (0-15 cm)	0.755
X_2, $Ca(H_2PO_4)_2$-HOAc-extractable S ppm (0-15 cm)	0.503
X_4, $CaCl_2$-extractable S ppm (0-15 cm)	0.092
X_{14}, Percent S in plant at early sampling	0.027
X_9, Soil P kg/ha	0.005

Appendix F. Standard Partial Regression Coefficients of All Variables Entered in Last Step of Zn Analysis (Early Sampling, Check Treatment).

Variable	Standardized Regression Coefficients
X_{10}, Soil Ca and Mg meq/100g (0-15 cm)	0.643
X_2, DTPA-extractable Zn ppm (0-15 cm)	1.749
X_9, Soil pH	0.334
X_{14}, Percent K in plant	-0.302
X_3, EDTA-extractable Zn ppm (0-15 cm)	-1.321
X_4, 0.1N HCl-extractable Zn ppm (0-15 cm)	-0.256
X_7, 0.1N HCl-extractable Zn ppm (0-61 cm)	0.029
X_{11}, Soil P kg/ha	0.222
X_8, Percent soil organic matter	0.347
X_6, EDTA-extractable Zn ppm (0-61 cm)	0.251
X_5, DTPA-extractable Zn ppm (0-61 cm)	-0.274
X_{12}, Percent N in plant	0.115
X_{15}, Percent S in plant	-0.014
X_{13}, Percent P in plant	-0.024

Appendix G. Standard Partial Regression Coefficients of All Variables Entered in Last Step of Zn Analysis (Late Sampling, Check Treatment).

Variable	Standardized Regression Coefficients
X_{15}, Percent S in plant	0.454
X_{14}, Percent K in plant	0.387
X_{10}, Soil Ca and Mg meq/100g (0-15 cm)	0.334
X_9, Soil pH	-0.646
X_7, 0.1N HCl-extractable Zn ppm (0-61 cm)	0.049
X_3, EDTA-extractable Zn ppm (0-15 cm)	-1.692
X_8, Percent soil organic matter	0.270
X_2, DTPA-extractable Zn ppm (0-15 cm)	0.110
X_4, 0.1N HCl-extractable Zn ppm (0-15 cm)	0.270
X_{11}, Soil P kg/ha	-0.233
X_{13}, Percent P in plant	0.265
X_{12}, Percent N in plant	0.264
X_{16}, Percent S in plant at early sampling	0.126
X_6, EDTA-extractable Zn ppm (0-61 cm)	0.083
X_5, DTPA-extractable Zn ppm (0-61 cm)	0.046

Appendix H. Standard Partial Regression Coefficients of All Variables Entered in Last Step of Zn Analysis (Early Sampling, Zn Treatment).

Variable	Standardized Regression Coefficients
X_{10}, Soil Ca and Mg meq/100g (0-15 cm)	0.624
X_7, 0.1N HCl-extractable Zn ppm (0-61 cm)	0.347
X_2, DTPA-extractable Zn ppm (0-15 cm)	-1.956
X_4, 0.1N HCl-extractable Zn ppm (0-15 cm)	0.290
X_{14}, Percent K in plant	0.037
X_8, Percent soil organic matter	-0.659
X_3, EDTA-extractable Zn ppm (0-15 cm)	1.787
X_{11}, Soil P kg/ha	-0.469
X_5, DTPA-extractable Zn ppm (0-61 cm)	0.439
X_6, EDTA-extractable Zn ppm (0-61 cm)	-0.167
X_{13}, Percent P in plant	-0.130
X_{12}, Percent N in plant	0.138
X_{15}, Percent S in plant	-0.104
X_9, Soil pH	-0.167

Appendix I. Standard Partial Regression Coefficients of All Variables Entered in Last Step of Zn Analysis (Late Sampling, Zn Treatment).

Variable	Standardized Regression Coefficients
X_{15}, Percent S in plant	0.174
X_{10}, Soil Ca and Mg meq/100g (0-15 cm)	0.647
X_{12}, Percent N in plant	0.566
X_{9}, Soil pH	0.584
X_{11}, Soil P kg/ha	0.389
X_{6}, EDTA-extractable Zn ppm (0-61 cm)	0.128
X_{5}, DTPA-extractable Zn ppm (0-61 cm)	0.075
X_{2}, DTPA-extractable Zn ppm (0-15 cm)	0.851
X_{14}, Percent K in plant	0.311
X_{4}, 0.1N HCl-extractable Zn ppm (0-15 cm)	0.425
X_{16}, Percent S in plant at early sampling	0.286
X_{13}, Percent P in plant	0.084
X_{8}, Percent soil organic matter	0.140
X_{3}, EDTA-extractable Zn ppm (0-15 cm)	0.082
X_{7}, 0.1N HCl-extractable Zn ppm (0-61 cm)	0.062